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- (54) Disperse and acid azo dyes having 1,2-dihydroquinoline couplers and heterocyclic diazos
- (57) New dyes of formula (I) give blue to green shades on polyamide fibres:

$$D-N=N-C' \qquad (I)$$

wherein C' is an optionally substituted 1,2-dihydroquinoline coupler, and D is selected from:

wherein rings I-IV are optionally substituted.

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SPECIFICATION

Disperse and acid azo dyes having 1,2-dihydroquinoline couplers and heterocyclic diazos

5 This invention concerns disperse and acid dyes particularly suited for the dyeing of polyamide fibres, and having the general formula

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$$D-N=N-C^1$$

10 wherein D is thiazol-2-yl, isothiazol-3-yl, 1,2,4-thiadiazol-5-yl or 1,3,4-thiadiazol-2-yl, each of which is unsubstituted or substituted with substituents such as acyl, acylamido, alkyl, SO₃M, carboalkoxy, halogen, cyano and alkyl-SO₃M, as defined below, and C¹ is a 1,2-dihydroquinoline coupler which is unsubstituted or substituted with such substituents as alkyl, aryl, alkyl-SO₃M, and substituted alklyl.

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More particularly, with regard to the above formula, D is selected from 15

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wherein the rings I-IV are either unsubstituted or substituted with substituents selected from alkył, alkoxy, halogen, alkylsulfonyl, SO₂NH₂, SO₂NHalkył, SO₃M, alkyl-SO₃M, SO₂N(alkyl)₂, arylsulfonyl, acylamido, aryl, arylthio, alkenylthio, cyclohexylthio, SO₃C₆H₅, cyano, thiocyano, 25 cyclohexylsulfonyl, alkylthio, nitro, formyl, alkanoyl, alkoxycarbonyl, aroyl, dialkylcarbamoyl, aroylamino alkylsulfonamido, CF3, carbamoyl, alkylcarbamoyl, and cyclohexyl, wherein the alkyl, alkenyl and cyclic moieties in said ring substituents may bear up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, cyclohexyl, furyl (C₄H₃O), aroyloxy, alkoxycarbonyl, alkanoyloxy, SO₂NH₂, SO₂NHaryl, SO₂NHalkyl, SO₂N-(alkyl)₂, 30 NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C4H4O2N), alkyl-SO3M, alutarimido (C_aH_aO₂N), phthalimido (C_aH₄O₂N), 1-(2-pyrrolidono) (C₄H₆ON), cyano, CONH₂,

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CONHalkyl, CON(alkyl)2, alkoxy-alkoxy, alkylthio, halogen, arylthio, alkylsulfonyl, arylsulfonyl, and aryloxy, and the coupler C1 has the formula

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wherein R, is H or a group selected from alkyl, aryl and cyclohexyl, which groups may themselves be substituted with 1-3 substituents different from the said group and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C₄H₃O), 45 aroyloxy, alkoxycarbonyl, alkanoyloxy, SO₂NH₂, SO₂NHaryl, SO₂NHalkyl, SO₂N-(alkyl)₂, NHCOOalkyl, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₈O₂N), phthalimido (C₈H₄O₂N), 1-(2-pyrrolidono) (C₄H₈ON), cyano, CONH₂, CONHalkyl, -SO₃M, alkyl-SO₃M, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsuifonyl and arylsulfonyl, R2 and R3 are each independently selected from H and alkyl, R4 is H, alkyl or alkyl-50 SO₃M, and R₅ is selected from H, alkyl, alkoxy, alkenyl of 2-6 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1-3 substituents independently selected from hydroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl,

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alkanoyloxy, and alkoxycarbonyl, wherein M is selected from H, Na, K, NH4,

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and the colorless cations of primary, secondary and tertiary aliphatic and aryl amines. The various alkyl moieties in, for example, alkoxy, alkanoyl and the like within the above definitions of R1, R5, and the D radical substituents preferably have 1-6 carbons, and they and the alkenyl groups are straight or branched chain. Any aryl moiety preferably has 6-10 ring carbon atoms.

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Preferred of the present dyes are where the substituents on the D rings are selected from 65 alkylthio, arylthio, cyclohexylthio, alkyl-SO₃M, cyanoalkyl, alkyl and halogen, R₁ is H, alkyl,

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hydroxyalkyl, alkanoyloxyalkyl or alkoxycarbonylalkyl, and $R_{\scriptscriptstyle 5}$ is H or alkyl.

The dyes of this invention impart blue to green shades on fibers, particularly polyamides, exhibiting improvements in fastness to one or more of light, ozone, perspiration, oxides of nitrogen, washing, sublimation and crocking, leveling, transfer, pH stability, exhaustion, build and diminished red flaring.

The diazo components used in this invention are prepared according to procedures well known to the art. The present disperse dyes may be applied to polyamide fibers by conventional dyeing procedures, e.g., dispersed in a lignin sulfonate and dyed at 98°C. on nylon fabric for one hour from an aqueous bath.

The acid dyes of the invention may be applied to polyamide fiber by the following method: The test dye, as a mixture with a sulphate such as ammonium sulfate, is pasted with boiling water and then made up to a known volume with water to give a weight ratio of water to dye of 30:1. Four percent on weight of fiber (owf) of a lignin sulphonate leveling agent is added, followed by ammonium acetate (about 3.0% owf) to adjust the pH to 6. The initial dyeing 15 temperature is 40°C. which is raised to the final dyeing temperature of 98°C. over 30 minutes. The dye bath is held at 98°C. for 60 minutes, then cooled, and the test fabric given a warm water rinse and air drying.

The following examples illustrate procedures which are generally applicable for preparation of the present couplers and dyes.

EXAMPLE 1

(a)—Preparation of 1,2-Dihydro-2,2,4,7-Tetramethylquinoline

Meta-toluidine (535 g.) and iodine (6 g.) are charged to a 2 liter, 3 neck, round bottom flask. The reaction is heated to 155°C. and about 3,500 g. of acetone is added at 155-160°C. 25 beneath the surface over a 12 hour period. A mixture of acetone and water distills off during the addition. The reaction mixture is heated one-half hour at 160°C, and then distilled to leave about 690 g. of 1,2-dihydro-2,2,4,7-tetramethylquinoline boiling at 107-111*C. at 0.55 mm., a 74% yield. This product is then ethylated with triethylphosphate in the presence of ethyl iodide.

30 (b)—Diazotization and Coupling Sodium nitrite (3.6 g.) is added portionwise to 25 ml. of concentrated H₂SO₄. The solution is cooled and 100 ml. of 1:5 acid (1 vol. propionic:5 vol. acetic) is added below 15°C. The mixture is cooled and 8.05 g. (0.05 m) of 2-amino-5-ethylthio-1,3,4-thiadiazole is added below 10°C. After stirring at 0-5°C. for one hour, the diazo solution is added to 1-ethyl-2,2,4,7-35 tetramethyl-1,2-dihydroquinoline (10.75 g., 0.05 mole) in 50% aqueous ethanol (54.0 cc.)

containing sodium acetate (2.05 g), at <5°C. After stirring at 0-5°C. for one hour the dye is warmed to room temperture and precipitated by adding to cold water. The product is filtered and washed well with water to yield the dye.

The preparation of the sulfonated 1,2-dihydro-quinoline is given in German Offen. 3,005,874 50 (C.A. 94, 15593K, 1981) and comprises sulfonating the 4-alkyl-1,2-dihydroquinoline with 50 H₂SO₄, CISO₃H, and/or SO₃ and converting, if desired, the acid group to its salt in known manner.

EXAMPLE 2

55 The diazonium from Example 1(b) is added to the potassium salt of 1-ethyl-2,2,7-trimethyl-1,2-dihydroquinoline-4-yl methyl sulfonic acid (0.01 mole) in water (11 cc.) at <5°C. After stirring at 0-5°C. for one hour the dye was warmed to room temperature and precipitated by adding to a saturated potassium chloride solution. The product was filtered and washed with diethyl ether, to yield the final dye product.

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The exemplary dyes of the following tables are prepared as in the above examples by procedural modifications if such are needed, as known to those skilled in the art.

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		TABLE 1		-	
-	S R R R R R R R R R R R R R R R R R R R	R and R and		HIT N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-	,
Substituent on Ring I or II None	. н. г.	R R		₄ [±]	. II
None	H	. CH ₃		.: cH ₃	c ₂ H ₅
CN	CH ₃ CH	сн _з сн _з	_	CH ₃	C3H7-n
сн ₃	сн ₂ сн ₂ он сь	сн3 сн3		ch ₂ so ₃ k	п- ₆ н ₉ -п
CH ₂ CH ₂ SCH ₃	СН ₂ С1 Н)нэ	сн(сн ₃) ₂	снз	CH ₂ CH ₂ -SO ₂ NHC ₆ H
$\mathrm{ch_2ch_2ch_2ch_2}$	осн ₂ с1 н	CH ₃		CH ₂ SO ₃ Na	Ch20C,H5
ch_2 ch(ch $_3$) $_2$	90СН3	z			G
C ₆ H ₄ -p-s0 ₃ K	н осн ₃ н	æ		$CH_2SO_3(Ca/2)$	C6H4-P-SO3K
C6H11	CH2CH2CN H	×		$CH_2SO_3(Zn/2)$	C ₆ H ₁₁
C ₆ H ₄ -o-Cl	C1 H	CH ₃		CH ₃	CH2CH2OC6H11
c ₆ հ ₄ -ո– c _H ₃	С1 н	CH ₃		CH ₂ SO ₃ NH ₄	CH2CH2SO2NH2
с ₆ н ₄ -р-осн ₃	H	CH ₃		CH ₃	сн ₂ сн ₂ он

Nepocini -GP

0C ₂ H ₅	осн ₃	c _H 3	снз	сн ₃	$\mathrm{CH}_2\mathrm{CH}_2\mathrm{SO}_2\mathrm{N}(\mathrm{C}_2\mathrm{H}_5)_2$
$\mathrm{CH}_2\mathrm{SO}_2\mathrm{NHCH}_3$	инсно	Эз	сн3	CH ₃	cH ₂ cH ₂ oc ₂ H ₅
$\text{CH}_2\text{SO}_2\text{NH}_2$	NHCOCH ₂ OCCH ₃	C4H9-n C4H9-n	C4H9-n	сн ₃	CH ₂ CN
сн200ссн3	NHCOCH ₂ CH ₃	C4H9-n	C4H9-n	#	CH2CONH2
сн ₂ соосн ₃	NHCOC ₂ H ₅	C4H9-n C4H9-n	0,449-n	×	CH ₂ CONHCH ₃
ch ₂ oocc ₆ H ₅	NHCOC ₆ H ₅	C3H2-11 (c3H2-n	ch ₂ ch ₂ so ₃ k	$cH_2con(c_2H_5)_2$
so ₂ nhch ₃	NHCOC ₂ H ₅	C3H7-n C3H7-n	C3H7-n	æ	CH ₂ NHCOCH ₃
$cH_2con(c_2H_5)_2$	NHCOC ₆ H ₁₁	C3H2-n	c3H7-n	CH2SO3N H(Et)3	CH ₂ NHCOOCH ₃
C1	н	сн3	CH ₃	н	сн ₂ 00ссн ₂ -s0 ₃ к
$cH_2cH_2(c_4H_30)$	CH ₂ SCH ₃	5 2	CH ₃	CH2SO3N HCH3(Ph)2 CH(C4H6ON)	CH(C,H,ON)
$so_2c_6H_{11}$	CH ₂ CH≈CH ₂	×	æ	H	ch ₂ ch ₂ cooch ₃
I	Br	=	c _H ³	сн3	$c \mu_2 c \mu_2 c o o c \mu_3$
Вт	ı.	æ	CH ₃	сн3	=
so ₂ cu ₃	<u>St</u>	æ	сн	$ch_2 so_3 K$	$\mathrm{cH_2cH_2c_2^{H_5}}$
so ₂ nH ₂	s сн ₃	×	CH ₃	CH ₃	C3H7-n
${\rm so_2}$ nhch $_2{\rm so_3}$ k	CH200CCH3	æ	снз	сн ₃	$c_2 H_5$

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${\rm so_2}^{\rm N(C_2H_5)_2}$	och ₃	Ξ	CH ₃	сн	CH,CH,C, H,
$\mathrm{so_2}$ nhch $_2$ ch $_2$ ch $_3$	c _H ³	×	CH ₃	. EHO	CH,C _c H,
$\mathrm{so_2^{CH}_2^{CH}_2^{OC}_2^{H}_5}$	сн3	Ξ	CH ₃	CH ₃	CH,C1
sc ₆ н ₅	сн2сн2соосн3	×	CHJ	ິສວ	, H, S
$sc_{6H_{11}}$	сн ₂ сн(он)сн ₂ он	æ	` £	ົ້ສິ	в э С _с н, -р-осн,
$^{\mathrm{S0}_{2}\mathrm{C}_{6}\mathrm{H}_{5}}$	cF_3	Ħ	CH ₃	CH ₃	C,H,AP-OH
$so_3c_6H_5$	cr ₃	Ŧ	CH ₃	CH ₃	CH, CH, SC, HE
sch ₂ ch ₂ on	33	CH ₃	СН3	сн	cornorno
sch2ch=ch2	H	сн3	CH ₃		CH ₂ CH ₃ SO ₂ C ₄ H ₅
$sch_2^{c00c_2^{H_4}-so_3^{K}}$	сн ₂ сн(с1)сн ₂ с1	CH3	CH.	CH ₃	C 0 7 7 7 CH"OC"H"
scH ₂ C ₆ H ₅	ch2ch(och3)ch2och3	CH3	CH,	CH,	CH_CN
$sch_2c_6H_{11}$	СНЭ	CH3	์ ผว	CH,SO,K	CH, (C, H, O, N)
sch2ch2oc2h5	CH ₃	, £	CH.	CH,	CH_CONHCH_
SCN	EE EE	CH,	์ ม	CH,	CH. CONCC. H.)
sch ₂ ch ₂ nhcoch ₃	Ħ	CH ₃	g E	CH,SO,Na	CH, NHCOCH,
$sch_2ch_2(c_4H_4o_2N)$	CH ₃	CH ₃	CH ₃	์ เมื	CH,NHCOOCH,
cH ₂ sc ₆ H ₅	сн ₂ сн ₂ он	CH ₃	CH ₃	CH ₃	сн ₂ 00ссн ₁
				ı	•

$c H_2 c H_2 s o_2 c H_3$	CH ₂ CI	сн 3	CH ₃	cH ₃	CH2(C4H60,N)
сн ₂ sо ₂ с ₆ н ₅	och ₂ c1	CH ₃	сн3	н	CH2CH2COOCH3
sch ₂ ch ₂ oc ₆ h ₅	осн	Н	CH ₃	×	CH ₂ CH ₂ COOCH ₃
sch ₂ ch ₃	осн	CH ₃	CH ₃	c_3H_7-n	сн,оосс, н
$cH_2(c_8H_4o_2N)$	CH2CH2CN	CH ₃	CH ₃	C3H2-n	C, H,
сн ₂ инсоинсн ₃	c1	CH3	CH.	C ₂ H ₅	C ₂ H _S
CH ₂ NHCOOCH ₃	×	CH ₃	CH ₃	$c_2^{H_5}$	C _H S
CH ₂ SO ₂ NHC ₆ H ₅	och ₃	сн3	CH.3	. CH ₃	C ₂ H ₅
$cH_2so_2N(c_2H_5)_2$	инсно .	×	æ	.	CH ³
sсн ₃	NHCOCH ₂ OCCH ₃	#	æ	H	c, H _S
$\mathrm{CH}_2(\mathrm{C}_4\mathrm{H}_4\mathrm{O}_2\mathrm{N})$	NHCOCH ₂ CH ₂ OCH ₃	CH ₃	CH ₃	CH ₃	C, H, 1
$\mathrm{CH}_2\mathrm{SO}_2\mathrm{NHCH}_3$	NHCOC ₂ H ₅	CH ₃	CH ₃	CH ₂ SO ₃ K	C,H ₅
${\rm CH_2CH_2NHCOCH_3}$	NHCOC ₆ H ₅	CH3	CH ₃	CH ₃	но но но
инсосн ₃	NHCOC ₂ H ₅	CH ₃	CH ₃	cH ₃	но'но'но
$cH_2cH_2(c_4H_6oN)$	NHCOC ₆ H ₁₁	CH ₃	CH ₃	CH ₂ SO ₃ NH ₄	сн ₂ сн ₂ он
Cen4-p-cn	Ħ	CH ₃	CH ₃	CH ₃	CH ₂ CH ₂ OC ₂ H ₅
CH ₂ CONH ₂	CH ₂ SCH ₃	CH3	CH ₃	CH ₃	CH ₂ CN

CH ₂ CONHCH ₃	ch ₂ ch≈ch ₂		CH ₃	СНЗ	CH2CONH2
	æ	æ	Ŧ	×	æ
	#		CH ₃	свз	$c_2^{H_5}$
	СН3		CH ₃	CH ₃	C ₂ H ₅
	сн ₂ сн ₂ он		CH ₃	сн ₃	C ₂ H ₅
	CH ₂ C1	=	сн(сн3)2	CH ₃	$c_{2^{H_5}}$
	och ₂ c1		CH ₃	CH2SO3NH4	c_2H_5
	cH ₃	×	z	Ħ	CH ₃
	осн ₃	æ	Ħ	сн ₂ сн ₂ so ₃ к	c ₆ H ₅
	CH ₂ CH ₂ CN	æ	=	Œ	C ₆ H ₁₁
	C1	×	снз	CH2SO3K	$c_2^{H_5}$
	C1	=	CH ₃	снз	сн2сн2он
$\mathrm{sch}_2\mathrm{ch}_3$	н	Ħ	Ħ	н	c H.
c ₆ H ₅	снз		снз	CH ₃ CH ₃	C Z COHE
0 1	CH ₃		CH ₃	C H	CH, CH, C, H,
сн ₃	CH ₃		OH,	Н	College College
$^{3}6^{\mathrm{H}}^{5}$	ch ₃	сн3	· ·	н	с 2 сн ₂ сн ₂ он

CH ₃ CH ₄ CH ₃ CH ₄	сн ₃ сн ₃		GH ₃	CH ₂ SO ₃ NH ₄ CH ₂ SO ₃ Na	сн ₂ с ₆ н ₅ с ₂ н ₅
	GH,	CH ₃		CH ₂ SO ₃ Na CH ₂ SO ₃ Na	$^{\mathrm{CH}_2\mathrm{CH}_2\mathrm{C}}_{6^{\mathrm{H}_5}}$
ij	۰ ۲ ۰	GH.		$^{2}_{\rm CH_{2}SO_{2}NHEt_{2}}$	CH ₂ CH ₂ OH
CH		CH ₃		CH ₂ SO ₃ K	$^{\mathrm{CH}}_{2}^{\mathrm{C}_{6}}$

		TABLE 2	E 2			
	Real IIII	R4 and	R III	Re IIV N -N=N-	2/ Z	
		× × × × × × × × × × × × × × × × × × ×	K ₇ s	R	R ₁	
. је	R7	² 2	R ₂	ا _ي ج	R ₄	R ₁
	= == :	H	æ	¥	×	=
=	æ	×	æ	сн3	CH ₃	c ₂ H ₅
C1	CN	CH ₃	CH ₃	СН3	ch ₃	c, H _c
Br	сн ₃	сн ₂ си ₂ он	CH ₃	CH ₃	CH ₃	CH,CH,SO,N(CH,),
сн ₃	сн2сн2sсн3	ch ₂ c1	=		CH, SO, K	C, H _E
CN	20C2H5	осн2с1	×		CH, SO, NH,	, a.c.
C ₂ H ₅		енэо	==		, , ,	CH,C,H,-p-SCH,
соосн3		осн ₃	=	æ	CH ₂ SO ₃ (Ca/2)	C, H + 0 2
CONH ₂	C ₆ H ₁₁	CH ₂ CH ₂ CN	×	æ	· =	, "H, S
$con(c_2H_5)_2$	C6H4-2-C1	c1	×	СН ₃	CH, SO, (Zn/2)	0 11 C,H,
CH ₂ 00C ₂ H ₅	с ₆ н ₄ - <u>е</u> -сн ₃	C1	×		C T HO	CH,CH,OH
с ^{6 н} 5	$c_6H_4-P-0cH_3$	æ	50	CH ₃	CH ₃	CH ₂ CH ₂ OH

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$c_{\rm H_2}c_{\rm H_2}s_{\rm CH_3}$	oc ₂ H ₅	осн3	CH ₃	CH ₃	сн	сн,сн,он
$\mathrm{ch_2ch_2och_2ch_2oc_2h_5}$	$ch_2 so_2$ nhch $_3$	инсно	GH ₃	CH ³	CH.	CH2CH2CH2
$c_{\rm H_2}c_{\rm H}(c_{\rm H_3})_2$	$\text{CH}_2\text{SO}_2\text{NH}_2$	инсосн ₂ оссн ₃	C4H9-ո	C4H9-n	CH ₃	CH ₂ CN
C ₆ H ₅	си ₂ оосси ₃	инсосн2сн3	C4H9-n	C4H9~n	· **	CH,CONH,
c_{6} H ₁₁	сн ₂ соосн ₃	NHCOC ₂ H ₅	c4H9-n	ս_6 _H ⁵ շ	æ	CH, CONHCH,
C ₆ H ₄ -o-C1	ch200cc6 ^{h5}	NHCOC ₆ H ₅	C3H7-n C3H7-n	c ₃ H ₇ -n	CH2CH2SO3K	CH2CON(C,Hs),
С ₆ Н ₄ - <u>ш</u> -сн ₃	so ₂ nhch ₃	NHCOC ₂ H ₅	C3H7-n	c_3H_7 -n	, #	CH ₂ NHCOCH ₃
с ₆ н ₄ - <u>р</u> -осн ₃	$cH_2con(c_2H_5)_2$	NHCOC ₆ H ₁₁	C3H7-n	c ₃ H ₇ -n	CH ₂ SO ₃ Na	CH ₂ NHC00CH ₂
oc ₂ H ₅	C1	æ	CH ₃	CH ₃) 	CH ₂ 000CH ₃
${\rm CH_2SO_2}{\rm NHCH_3}$	CH2CH2(C4H30)	сн ₂ sсн ₃	Ŧ	CH ₃	CH ₂ SO ₃ N H(Et) ₃	CH(C ₄ H ₆ ON)
CH ₂ SO ₂ NH ₂	$so_2c_6H_{11}$	CH ₂ CH=CH ₂	æ	=	===	сн, сн, соосн
сн ₂ 00ссн ₃	н	Br		CH ₃	CH3	CH,COOCH,
$c_{H_2}c_{00}c_{H_2}s_{0_3}\kappa$	Вг	ı	æ	CH ₃	CH ₃	· =
сн ₂ 00сс ₆ н ₅	so ₂ cH ₃	Œ,	H	E	CH ₂ SO ₃ K	2,H ₅
so ₂ nhch ₃	so ₂ nH ₂	sch ₃	æ	CH.3	CH ₃	c ₂ H ₅
$cH_2con(c_2H_5)_2$	so ₂ nhch ₂ so ₃ k	сн2000сн3	=	CH ₃	сн ₃	$c_2^{\mathrm{H}_5}$
C1	$so_2^{M(C_2H_5)_2}$	och ₃	æ	CH ₃	CH2SO3NH4	$c_2^{H_5}$

$c_{\rm H_2} c_{\rm H_2} (c_4^{\rm H_3} o)$	So_2 nhch $_2$ ch $_2$ ch $_2$ och $_3$	снз	æ	CH ₃	CH ₃	C2H5
$^{\text{CH}_2}(c_8^{\text{H}_4^{\text{O}_2^{\text{N}}}})$	$\mathrm{so_2^{cH}}_{2}^{\mathrm{cH}_2}^{\mathrm{oc_2}}^{\mathrm{H}_5}$	снз	æ	CH ₃	cH ₃	CH ₃
сн ₂ инсоинсн ₃	sc ⁶ H ²	сн ₂ сн ₂ соосн ₃	Ħ	CH ₃	CH ³	c H ₅
CH ₂ NHCOOCH ₃	sc ₆ H ₁₁ .	сн ₂ сн(он)сн ₂ он	Ξ	CH ₃	CH,	Cen 1
CH ₂ SO ₂ NHC ₆ H ₅	${ m so_2c_6 H_5}$	CF ₃	æ	CH3	CH ₂ SO ₃ Na	C ₂ H ₅
$c_{\mathrm{H}_2} s_{\mathrm{O}_2} N (c_2 H_5)_2$	so ₃ c ₆ _{H5}	CF ₃	×	CR3	CH ₃	си2си2он
SCH ₃	sch ₂ ch ₂ oн	H	CH ₃	CH3	cH ₃	ch ₂ ch ₂ on
$\mathrm{CH}_2(\mathrm{C}_4\mathrm{H}_4\mathrm{O}_2\mathrm{N})$	sch ₂ ch=ch ₂	#	CH ₃	cg,	cH ₃	но сн сн с
CH ₂ SO ₂ NHCH ₃	$sch_2cooc_2H_5$	сн ₂ сн(с1)сн ₂ с1	сн3	сн ³	cH ³	ຳ
CH ₂ CH ₂ NHCOCH ₃	$\mathrm{sch_2c_6H_5}$	ch2ch(och3)ch2och3	CH ₃	CH ₃	CH ₃	CH ² CN
NHCOCH ₃	$sch_2c_6H_{11}$	CH ₃	CH ₃	CH	CH ₃	ch,conh,
$cH_2cH_2(c_4H_6oN)$	sch ₂ ch ₂ oc ₂ h ₅	CH ₃	CH ₃	CH ₃	CH ₂ SO ₃ K	HOHNOO'HO
C ₆ H ₄ -p- cn	SCN	æ	CH ₃	сн ³	. E	CH,CON(C,H,)
CH ₂ CONH ₂	sch ₂ ch ₂ nhcoch ₃	н	CH ₃	E	์ เมื	CH, NHCOCH,
CH ₂ CONHCH ₃	$\mathrm{sch}_2\mathrm{ch}_2(\mathrm{c}_4\mathrm{H}_4\mathrm{o}_2\mathrm{N})$	CH ₃	CH ₃	CH ₃	CH ₃	сн, инсоосн
×	cH2sc6H5	сн2сн2он	CH3	CH3	c _B 3	с 7
æ	сн ₂ сн ₂ so ₂ сн ₃	CH ₂ C1	CH ₃	CH ₃	CH ₃	$cH_2(c_4H_6o_2N)$

c1	CH2SO2C6H5	OCH ₂ C1	CH ₃	CH ₃	ж	$\mathrm{ch_2ch_2cooch_3}$
Вг	sch ₂ ch ₂ oc ₆ h ₅	осн ₃	CH ₃	CH ₃	æ	сн2сн2соосн3
сн ₃	sch ₂ ch ₃	оснз	СН3	CH3	C3H7-n	æ
CN	$CH_2(C_8H_4O_2N)$	CH2CH2CN	CH3	сн3	$c_3H_7^{-n}$	c ₂ H ₅
$c_2 H_5$	CH ₂ NHCONHCH ₃	c1	CH ₃	CH ₃	c ₂ H ₅	c ₂ H ₅
соосн	сн ₂ инсоосн ₃	22	CH3	CH ₃	$c_2^{H_5}$	$c_2^{H_5}$
CONH ₂	CH ₂ SO ₂ NHC ₆ H ₅	осн ₃	CH ₃	CH ₃	CH ₃	C ₆ H ₄ -0, p-d1-c1
$con(c_2H_5)_2$	$cH_2 so_2 N (c_2 H_5)_2$	NHCHO	æ	=	=	сн ₃
$\mathrm{GH_200C_2H_5}$	scн ₃	NHCOCH ₂ OCCH ₃	pr:	===	æ	c ₆ H ₅
c ₆ H ₅	$cH_2(c_4H_4o_2N)$	$^{\mathrm{NHCOCH}_2\mathrm{CH}_2\mathrm{OCH}_3}$	CH ₃	CH ₃	CH2SO3K	C ₆ H ₁₀ -P-c1
сн ₂ сн ₂ sсн ₃	$\mathrm{CH}_2\mathrm{SO}_2\mathrm{NHCH}_3$	NHCOC2H5	CH ₃	СНЭ	GH3	C ₂ H ₅
$c_{\rm H_2}c_{\rm H_2}c_{\rm H_2}c_{\rm H_3}$	CH ₂ CH ₂ NHCOCH ₃	NHCOC ₆ H ₅	CH ₃	CH ₃	CH ₃	си2си20н
$\mathrm{CH}_2\mathrm{CH}(\mathrm{CH}_3)_2$	инсосн ₃	NHCOC ₂ H ₅	CH ₃	cH ₃	CH2SO3K	CH2CH20H
C ₆ H ₅	$\mathrm{CH_2CH_2}(\mathrm{C_4H_6ON})$	$^{\mathrm{MCOC}_{6}}_{11}$	CH ₃	CH ₃	CH ₃	сн2сн2он
C6H11	C6H4-P-CN	æ	CH ₃	CH ₃	СНЗ	CH2CH2OC2H5
C ₆ H ₄ -o-c1	ch ₂ conh ₂	сн ₂ sсн ₃	CH ₃	Н	сн3	CH ₂ CN
C6H4-m-CH3	CH ₂ CONHCH ₃	cH ₂ cH=cH ₂	CH ₃	CH ₃	снз	CH2CONH2

с ₆ н ₄ -р-осн ₃	NO ₂	#	Ħ	æ	æ	.
	СНО	H	Ħ	CH ₃	сн3 сн3	$c_2^{\mathrm{H}_5}$
	сосн ³	сн ³	CH ²	CH ₃	CH ³	C3H7-n
	соосн3	сн2 сн2 он	CH ₃	CH ₃	CH ₃	C4 H9-n
	COC H ²	$c_{\rm H_2}c_{\rm I}$	£	CH(CH ₃) ₂	CH ₃	$c_2^{H_5}$
	NHCOC ₆ H ₅	осн ₂ с1	æ	CH ₃	CH ₂ SO ₃ K	$c_2^{H_5}$
	NHSO ₂ CH ₃	оснз	×	z	æ	CH
	c_{F_3}	осн3	æ	Ħ	æ	c, H ₅
$_{\rm CH_2}$ con($_{\rm C_2}$ $_{\rm H_5}$) $_{\rm 2}$	CONH2	CH2 CH2 CN	æ	×	æ	c_{6} H ₁₁
	CONHCH3	C1	Ħ	CH ₃	CH ₂ SO ₃ NH ₄	C ₂ H ₅
сн ² сн ² (с ⁴ н ³ о)	$\cos(c_2 H_5)_2$	C1	×	CH ₃	CH ₃	сн, сн, он

^{с2 н5} ^{с3 н5} ^{с4 с6 н5} ^{с6 н5} CH3
CH3
CH3
CH3
CH3
CH2
CH2
CH2SO3NA
CH CH3 H CH3 H CH3 H CH3 H CH3 CL Br COOCH₃ COOCH₃ CI CI CI CI CI COOCH₃ COOCH₃ COOCH₃

CLAIMS

1. A dye of the formula $D - N = N - C^{\dagger}$ wherein D is selected from

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wherein the rings I–IV are either unsubstituted or substituted with substitutents selected from alkyl, alkoxy, halogen, alkylsulfonyl, SO₂NH₂, SO₂NHalkyl, SO₂N(alkyl)₂, arylsulfonyl, acylamido, aryl, arylthio, alkenylthio, cyclohexylthio, SO₃M, alkyl-SO₃M, SO₃C₆H₅, cyano, thiocyano, cyclohexyl-sulfonyl, alkylthio, nitro, formyl, alkanoyl, alkoxycarbonyl, aroyl, dialkylcarbamoyl, aroylamino, alkylsulfonamido, CF₃, carbamoyl, alkylcarbamoyl, and cyclohexyl, wherein the alkyl, alkenyl and cyclic moities in said ring substituents may bear up to three substituents different from the moiety and independently selected from hydroxy, alkyl, alkoxy, aryl, SO₃M, alkyl-SO₃M, cyclohexyl, furyl, (C₄H₃O), aroyloxy, alkoxy carbonyl, alkanoyloxy, SO₂NH₃, SO₂N-

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alkyl-SO₃M, cyclohexyl, furyl, (C₄H₂O), aroyloxy, alkoxy carbonyl, alkanoyloxy, SO₂NH₂, SO₂N-Haryl, SO₂NH-alkyl, SO₂N(alkyl)₂, NHCOOalkyl, NHCONHalkyl, acylamido, alkysulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₅O₂N), phthalimido (C₈H₄O₂N), 1-(2-pyrrolidono) (C₄H₆ON), cyano, CONH₂, CONHalkyl, CON-(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl, arylsulfonyl, and aryloxy wherein M is selected from H, Na, K, NH₄,

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and the colorless cations of salts of primary, secondary and tertiary aliphatic and aryl amines, and wherein C¹ is a substituted or unsubstituted 1,2-dihydroquinoline radical.

2. A dye according to Claim 1 wherein the coupler C has the formula

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wherein R₁ is H or a group selected from alkyl, aryl and cyclohexyl, which groups may themselves be substituted with 1–3 substituents different from the said group and independently selected from hydroxy, alkoxy, aryl, aryloxy, cyclohexyl, cyclohexoxy, furyl (C₄H₃O), aroyloxy, alkoxy-carbonyl, alkanoyloxy, SO₂NH₂, SO₂NHaryl, SO₂NHalkyl, SO₂N(alkyl)₂, NHCOOalkyl, SO₃M, alkyl-SO₃M, NHCONHalkyl, acylamido, alkylsulfonamido, succinimido (C₄H₄O₂N), glutarimido (C₅H₆O₂N), phthalimido (C₈H₄O₂N), 1-(2-pyrrolidono) (C₄H₆ON), cyano, CONH₂, CONHalkyl, CON(alkyl)₂, alkoxyalkoxy, alkylthio, halogen, arylthio, alkylsulfonyl and arylsulfonyl, R₂ and R₃ are each independently selected from H and alkyl, R₄ is H, alkyl or alkyl-SO₃M, and R₅ is selected from H, alkyl, alkoxy, alkenyl of 2–6 carbons, halogen, acylamido, alkylthio and formamido, wherein the alkyl moieties thereof may be substituted with 1–3 substituents independently selected from hyroxy, halogen, cyano, alkoxy, alkylthio, alkanoyl,

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50 alkanoyloxy, and alkoxycarbonyl.
3. A dye according to Claim 2 wherein the substituents on the D rings are selected from alkylthio, arylthio, cyclohexylthio, alkyl-SO₃M, cyanoalkyl, alkyl and halogen, R₁ is H, alkyl, hydroxyalkyl, alkanoyloxyalkyl or alkoxycarbonylalkyl, and R₅ is H or alkyl.

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4. The dye according to Claim 1 of the formula 55

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65 5. The dye according to Claim 1 of the formula

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10. The dye according to Claim 1 of the formula

11. The dye according to Claim 1 of the formula

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12. The dye according to Claim 1 of the formula

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17. The dye according to Claim 1 of the formula

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18. The dye according to Claim 1 of the formula

19. The dye according to Claim 1 of the formula

20. The dye according to Claim 1 of the formula 35

45 21. The dye according to Claim 1 of the formula 45

55 22. The dye according to Claim 1 of the formula

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23. The dye according to Claim 1 of the formula

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24. The dye according to Claim 1 of the formula

25. The dye according to Claim 1 of the formula
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45 26. The dye according to Claim 1 of the formula 45

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65 27. The dye according to Claim 1 of the formula 65

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28. The dye according to Claim 1 of the formula

29. The dye according to Claim 1 of the formula

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